# Environmentally Sustainable Yellow Smoke Formulations for Use in the M194 Hand Held Signal

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## ABSTRACT

The burning of aerial pyrotechnic devices poses a public health risk as chemicals may be released into the water supply from solid fallout and surface water runoff. In the case of colored smoke signals, the risk is especially high because many colored smoke formulations contain highly toxic dyes that are not consumed by the key reduction-oxidation reaction. For the M194 yellow smoke hand held signal (HHS), the current in-service formulation contains two toxic anthraquinone dyes, namely benzanthrone and vat yellow 4 (VY4). To minimize the environmental impact of the M194 yellow smoke formulation, the present study aimed to replace the anthraquinone dyes with the more environmentally sustainable solvent yellow 33 (SY33). SY33, a quinoline dye that is currently used in colored smoke grenade production, has been deemed admissible by the U.S. Army Public Health Command (PHC). Several new yellow smoke formulations have been developed that meet the performance parameters (burn time, smoke output) of the M194, while providing an environmentally acceptable alternative to the current in-service formulation.

## Introduction

Hand held signals (HHS) are used to signal troop location and distress during combat operations, serving as a beacon for rescuers to identify the general location of military personnel.[1] Launched during daytime operations, smoke HHS are a means of tactical signaling complementary to illuminant HHS, which are typically launched during nighttime operations.[2] Because they are deployed during close combat situations, the formulation in colored smoke HHS must be robust enough to perform its intended function while not posing risk to the soldier or the environment. Chemical formulations in colored smoke HHS have the disadvantage of generating large amounts of toxic by-products, particularly the colored dyes that are not consumed by the key pyrotechnic reaction.[3]

Figure 1 shows the full-up system hardware for the M194 yellow smoke HHS, including the rocket motor, signal assembly, and parachute. Upon striking the primer by the firing pin in the palm of the hand, an initiating charge burns to ignite the rocket propellant and a delay element, sending the signal assembly airborne. As the assembly reaches its apex (an average height of ~725 feet), the burning of the delay element (5-6 seconds) then ignites an expelling charge to eject and light the yellow smoke candle. Suspended from a parachute during descent, the candle will burn for 9-18 seconds to generate a highly visible cloud of yellow smoke before burnout at 500-600 feet.

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**The burning of aerial pyrotechnic devices poses a public health risk as chemicals may be released into the water supply from solid fallout and surface water runoff. In the case of colored smoke signals, the risk is especially high because many colored smoke formulations contain highly toxic dyes that are not consumed by the key reduction-oxidation reaction. For the M194 yellow smoke hand held signal (HHS), the current in-service formulation contains two toxic anthraquinone dyes, namely benzanthrone and vat yellow 4 (VY4). To minimize the environmental impact of the M194 yellow smoke formulation, the present study aimed to replace the anthraquinone dyes with the more environmentally sustainable solvent yellow 33 (SY33). SY33, a quinoline dye that is currently used in colored smoke grenade production, has been deemed admissible by the U.S. Army Public Health Command (PHC). Several new yellow smoke formulations have been developed that meet the performance parameters (burn time, smoke output) of the M194, while providing an environmentally acceptable alternative to the current in-service formulation.**

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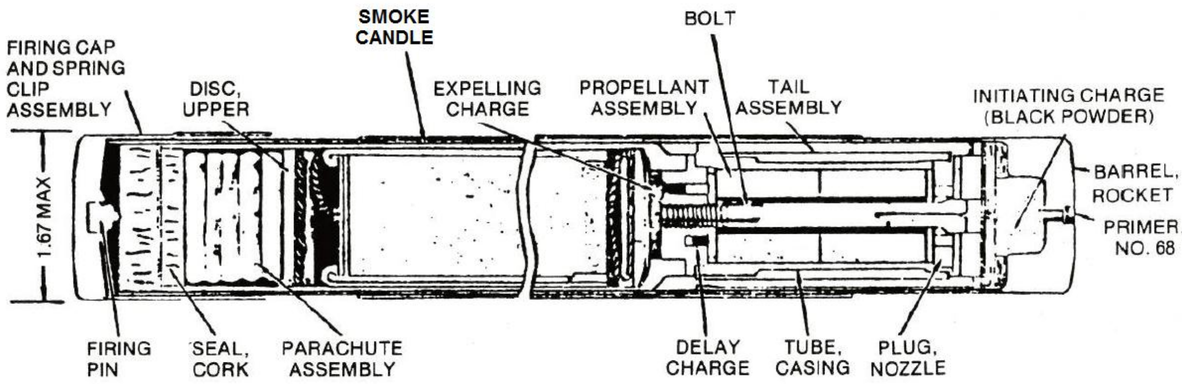


**Figure 1:** Cross-sectional diagram of the M194 HHS

Table 1 details the pyrotechnic formulation currently specified in the M194 technical data package. Upon initiation of the primer and propagation of the pyrotechnic train through the system hardware, potassium chlorate (oxidizer) and the sugar (fuel, or reducing agent) engage in a reduction-oxidation (redox) reaction to generate substantial heat. The heat, in turn, causes the dye molecules – vat yellow 4 (VY4) and benzanthrone – to enter the gas phase (sublimation). After dispersion of the dye molecules, contact with the cool ambient air causes them to condense to the solid phase to generate a visible cloud of yellow smoke. The rate and temperature of burning are partially controlled by sodium bicarbonate, which functions by an evaporative cooling mechanism.[3] Lastly, the entire formulation is "glued" together with vinyl alcohol acetate resin (VAAR) as a binder.

**Table 1:** Composition of M194 control formulation

| Ingredient | Wt. % | Function |
|---|---|---|
| Potassium Chlorate | 35.0 | Oxidizer |
| Sugar (sucrose) | 20.0 | Fuel |
| Vat yellow 4 | 13.0 | Smoke agent |
| Benzanthrone | 28.0 | Smoke agent |
| Sodium bicarbonate | 3.0 | Coolant |
| VAAR | 1.0 | Binder |

Although the M194 control formulation meets the performance requirement, the M194 yellow smoke HHS was discontinued during the early 1980s partly because of health concerns associated with VY4 and benzanthrone. Both of these compounds are anthraquinone dyes, and their structures are shown in Figure 2. Benzanthrone is a known dermal sensitizer, and is also reported to cause liver and nervous system damage, and therefore presents some occupational health issues. Oral toxicity to mammals is only moderate but is high to aquatic species low on the food chain, thereby rendering potential impacts on the ecosystem. On the other hand, VY4 is likely to contain small amounts of dibenzochrysene, an extremely potent carcinogen, in technical grade preparations.[4] Furthermore, VY4 is classified as a Group 3 material according to the International Agency for Research on Cancer (IARC) because evidence of this compound as a carcinogen remains inconclusive.[5]

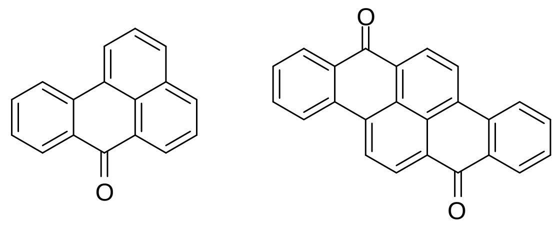


**Figure 2**: Structural formulae of yellow dyes present in the M194 baseline formulation

Recently, the U.S. Army Maneuver Center of Excellence (MCoE) has expressed a future demand in training and combat inventories for colored smoke HHS, including the M194.[6] In particular, MCoE has placed emphasis on making these products more environmentally sound and safer for the soldier. To meet this demand, new short-burning colored smoke formulations need to be developed to meet the specifications of each signal.

## Experimental Section

### *1. Materials*

Potassium chlorate, potassium nitrate, sodium bicarbonate, stearic acid, and sugar were purchased from Hummel Croton, Inc. Solvent yellow 33 was purchased from Nation Ford Chemical, Inc. Polyvinyl alcohol was purchased from Fisher Scientific, Inc. Nitrocellulose (NC) was purchased from Alliant Techsystems, Inc. Magnesium carbonate was obtained from Pine Bluff Arsenal (Pine Bluff, AR). All formulations were encased in uncoated kraft fiberboard tubes purchased from Security Signals, Inc.

### *2. Preparation of Yellow Smoke Formulations*

After oven-drying potassium chlorate overnight at 60 °C, formulations were prepared in 300 g batches by blending all ingredients according to their respective weight percentages shown in the formulation tables. Formulations containing only solid ingredients were tumbled end-over-end in conductive plastic containers for 60 min, while those containing NC or VAAR were blended in a Hobart mixer for 30 min. Dry-tumbled formulations were taken directly to loading operations without further processing, while NC- and VAAR-based formulations were oven-cured overnight at 60 °C prior to loading.

Blended formulations were weighed out in three 24-g increments and pressed into non-coated Kraft cardboard tubes (length of 4.93 cm, inner diameter of 0.838 cm), with the aid of a tooling die and a manual hand press, using a consolidation dead load of 2,177 kg. Between 68.9-71.7 g of energetic material was used per pellet, and 4 pellets were tested for each formulation. The top and inner core surfaces of each pellet were coated with a thin layer of first-fire composition. Pellets were remotely ignited with an electric match.

### *3. Characterization*

Data presented reflect average values calculated from measurement of 4 pellets per formulation. Burn times were measured (in seconds, s) from video recordings of burning samples. Accordingly, linear burning rates (in/s) and mass consumption rates (g/s) were calculated based on the lengths and weights of the consolidated formulations.

## Results and Discussion

To address the Army's future demand for parachute colored smoke HHS, a program was initiated by Armament Research, Development and Engineering Center (ARDEC) to develop environmentally benign yellow smoke formulations containing an alternate yellow dye – solvent yellow 33 (SY33, otherwise known as D&C Yellow No. 11). As shown below in Figure 3, the structure of SY33 consists of a quinoline carbon skeleton and may be described as 2-(2-quinolyl)-1,3-indandione. Although some toxicity concerns exist with SY33,[7] its use in a variety of industries is ubiquitous. In particular, it has been approved by the U.S. Food and Drug Administration (FDA) for use in cosmetics[8] and topical drugs.[9] Other industrial applications include use as a dye in spirit lacquers, polystyrene, polycarbonates, polyamides, acrylic resins, and hydrocarbon solvents. Most importantly, SY33 has been deemed admissible by the U.S. Army Public Health Command (PHC) in colored smoke formulations and this dye is presently used in M18 smoke grenade production.[4] Inhalation studies of SY33 as a smoke dye indicate that this compound is cleared from the lungs very rapidly.[10-13]

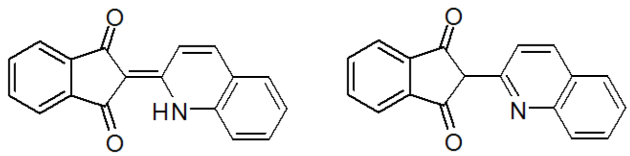

**Figure 3**: Tautomeric structural formulae of SY33

With an acceptable replacement dye in hand, formulation studies were executed to leverage an existing yellow smoke formulation developed previously during a product improvement program for the yellow smoke battlefield effects simulator (BES). As shown in Table 2, this formulation contains many of the same ingredients as the M194 baseline, only now SY33 serves as the smoke agent in place of benzanthrone and VY4. Also, magnesium carbonate is used as a coolant instead of sodium bicarbonate and stearic acid is introduced as a lubricant to assist processing. It was expected that modification of the BES formulation would lead to a new formulation that meets the burn time requirement of 9-18 seconds.

**Table 2**: Yellow smoke BES formulation

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 22.0 |
| Solvent yellow 33 | 31.0 |
| Magnesium carbonate | 15.5 |
| Stearic acid | 1.0 |
| VAAR | 1.0 |

The initial task was to prepare and test new yellow smoke formulations in parallel with the BES formulation. Table 3 below describes three binder study formulations A-C. Two of these formulations replace the binder system of the BES formulation with nitrocellulose (NC, formulation A) or polyvinyl alcohol (PVA, formulation B). Formulation C is a binder-free variant of A, with a corresponding 1 wt. % increase in SY33.

**Table 3**: Binder study formulations A, B, and C

**Formulation A**

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 22.0 |
| Solvent yellow 33 | 31.0 |
| Magnesium carbonate | 15.5 |
| Stearic acid | 1.0 |
| Nitrocellulose | 1.0 |

**Formulation B**

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 22.0 |
| Solvent yellow 33 | 31.0 |
| Magnesium carbonate | 15.5 |
| Stearic acid | 1.0 |
| Polyvinyl alcohol | 1.0 |

**Formulation C**

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 22.0 |
| Solvent yellow 33 | 32.0 |
| Magnesium carbonate | 15.5 |
| Stearic acid | 1.0 |

Table 4 below shows additional tolerance experiments modeled after the BES formulation. It was believed that altering ingredient ratios would reveal important relationships between them, and assist in reaching the target burn time. In particular, it was expected that the burn time of new formulations would be most sensitive to the coolant concentration. This proposition was based on the well-known fact that metal carbonates, decomposing endothermically, function as efficient burn rate retardants.[3] Therefore, several new formulations having coolant levels lower than than the BES were considered. Relative to the BES control, the sugar content of formulations D and E was increased at the expense of the coolant (magnesium carbonate). For formulations G and H, however, the dye content was increased at the expense of the coolant. Lastly, for formulation H, the magnesium carbonate present in BES was substituted with sodium bicarbonate.

**Table 4:** Tolerance study formulations

**Formulation D**

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 27.0 |
| Solvent yellow 33 | 31.0 |
| Magnesium carbonate | 10.5 |
| Stearic acid | 1.0 |
| VAAR | 1.0 |

**Formulation E**

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 32.0 |
| Solvent yellow 33 | 31.0 |
| Magnesium carbonate | 5.5 |
| Stearic acid | 1.0 |
| VAAR | 1.0 |

**Formulation F**

| Ingredient | Wt. % |
|---|---|
| Potassium chlorate | 29.5 |
| Sugar (sucrose) | 22.0 |
| Solvent yellow 33 | 36.0 |
| Magnesium carbonate | 10.5 |
| Stearic acid | 1.0 |
| VAAR | 1.0 |

**Table 4** (cont'd): Tolerance study formulations

| Formulation G | | Formulation H | |
|---|---|---|---|
| Ingredient | Wt. % | Ingredient | Wt. % |
| Potassium chlorate | 29.5 | Potassium chlorate | 29.5 |
| Sugar (sucrose) | 22 | Sugar (sucrose) | 22 |
| Solvent yellow 33 | 41 | Solvent yellow 33 | 31 |
| Magnesium carbonate | 5.5 | Sodium bicarbonate | 15.5 |
| Stearic acid | 1 | Stearic acid | 1 |
| VAAR | 1 | VAAR | 1 |

The table in Figure 4 below summarizes the performance of each formulation compared to the BES control. The visible smoke cloud generated by the BES control is representative for all formulations and is shown at the right in Figure 1. From the table it is clear that the BES formulation gave a burn time (37.5 s) far outside the specified range of 9-18 s. However, replacing the binder present in BES (formulations A and B) or eliminating it altogether (formulation C) gave much shorter burn times (<18 s in each case). The burn times of new formulations did not vary appreciably with the content of the potassium chlorate. As evidenced by formulations D and E, incrementally increased oxidizer content yielded burn times more-or-less equivalent to that of the BES control. Similarly, increased dye content of formulations F and G yielded burn times that were both longer than the BES control. Lastly, exchanging one coolant (magnesium carbonate) for another (sodium bicarbonate) corresponded to an appreciable improvement in burn time, demonstrated by formulation H.

**Figure 4:** Characterization of yellow smoke formulations

| Formulation | Burn Time (s) | Burn Rate (in/s) | Burn Rate (g/s) |
|---|---|---|---|
| BES control | 37.5 | 0.07 | 1.84 |
| A | 18.8 | 0.14 | 3.68 |
| B | 17.8 | 0.15 | 3.88 |
| C | 17.3 | 0.16 | 4.05 |
| D | 42.3 | 0.06 | 1.65 |
| E | 34.0 | 0.08 | 2.12 |
| F | 43.0 | 0.06 | 1.64 |
| G | 44.5 | 0.06 | 1.59 |
| H | 21.5 | 0.11 | 3.25 |

## Conclusions

In summary, several new formulations have been prepared and tested in support of a product improvement program for the M194 yellow smoke HHS. Important relationships were established by probing the tolerance of a control formulation to different ingredients and different ingredient percentages. Three formulations exhibited burn times within the specifications for the M194. Efforts to further shorten the burn times of new candidate formulations are presently ongoing in our laboratories.

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## References

1 J.J. Sabatini, et al. "Applications of High Nitrogen Energetics in Pyrotechnics: Development of Perchlorate-Free Red Star M126A1Hand-Held Signal Formulations with Superior Luminous Intensities and Burn Times." *Propellants, Explos. Pyrotech.* **2011**, *36*, 373 – 378.
2 A.A. Shidlovskiy, *Principles of Pyrotechnics*, 4th ed., Moscow, 1973. (Translated by Leo Kanner Associates, Redwood City, CA, 1974).
3 J.A. Conkling, C.J. Mocella. *Chemistry of Pyrotechnics: Basic Principles and Theory*, 2nd ed.; CRC Press, Taylor & Francis Group: Boca Raton, 2011.
4 Letter from Dr. William Eck to Daniel Colotti. "Informal toxicity comments on smoke components." U.S. Army Public Health Command, 2009.
5 International Agency for Research on Cancer (IARC). "Agents Classified by the *IARC Monographs*, Volumes 1–104," available via the Internet at http://monographs.iarc.fr/ENG/Classification/index.php.
6 Letter from Christopher Kennedy to Daniel Colotti. "Endorsement for Parachute Smoke Signals (Yellow M194, Green M128A1, and Red M129A1)." U.S. Army Maneuver Center of Excellence, 2010.
7 "Toxicology and Carcinogenesis of D&C Yellow No. 11in F344/N Rats (Feed Studies)," National Toxicology Program (NTP), April 1997.
8 "Color additives listed for use in cosmetics," Electronic Code of Federal Regulations, Title 21, Part 74, Subpart C.
9 "Color additives listed for use in drugs," Electronic Code of Federal Regulations, Title 21, Part 74, Subpart B.
10 T.C. Marrs, et al. "Inhalation Toxicity of a Smoke Containing Solvent Yellow 33, Disperse 9, and Solvent Green 3 in Laboratory Animals." *Human and Experimental Toxicology*, **1984**, *3*, 289-308.
11 M.A. Medinsky, et al. "Disposition and metabolism of $^{14}$-C-solvent yellow and solvent green aerosols after inhalation." *Fund. Appl. Toxicol.*, **1986**, *7*, 170-178.
12 J.D. Sun, et al. "The inhalation toxicity of two commercial dyes: Solvent yellow 33 and Solvent Green 3." *Fund. Appl. Toxicol.*, **1987**, *8*, 358-371.
13 T.C. Marrs, et al. "Inhalation Toxicity of a Coloured Smoke and the mutagenicity of its constituent dyes, solvent yellow 33 (CI 47,000) and disperse orange (CI 60,700)." *J. Hazard Mater.*, **1988**, *17*, 269-285.